AIR QUALITY

DRYDEN

Annual Report, 1978

Ontario
Ministry of the Environment

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TECHNICAL SUPPORT SECTION
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SUMMARY

Air quality investigations in Dryden, begun in 1970 by the Ontario Ministry of the Environment, continued in 1978 with vegetation and soil studies, a snow sampling survey, and measurements of dustfall, sulphation rates and total reduced sulphur.

Mercury persisted at concentrations slightly above normal in vegetation, soil, experimentally exposed moss, and snow in the immediate vicinity of a local chlor-alkali plant which had been converted from a mercury to a non-mercury process in late 1975. Our investigations indicated, however, that residual airborne mercury around the chlor-alkali plant and adjacent kraft pulp was not a cause for concern.

Particulate fallout around the pulp mill was evaluated by dustfall measurements, exposure of moss samples, and snow sampling. Total dustfall levels were usually acceptable or only marginally above the Ontario air quality objectives. Road dust, rather than emissions from mill operations, were suspected as the cause of some of the conspicuously high readings. Calcium was low in dustfall but elevated in moss and snow near the mill. Calcium in the 1978 snow samples was, however, much lower than that for 1977. Chloride was low in dustfall and only slightly above normal in moss exposed near the mill. Both sodium and sulphate in snow declined sharply from 1977 to 1978 as a result of emission controls brought into operation at the mill in early 1977. Sodium and sulphate were also very low in dustfall. The Ministry's 1978 monitoring results indicated that the discharge of particulate matter from the mill had decreased to the point where it no longer contributed significantly to dustfall in Dryden.

Odour levels, caused by emissions of total reduced sulphur (TRS) compounds from the mill, continued to be recorded at unacceptably high concentrations in 1978. The Ontario guideline for TRS was exceeded 400 times during the year, with the highest hourly concentration nearly 18 times the maximum acceptable value. TRS reached levels where some local residents might have experienced symptoms of temporary discomfort. The Ministry is currently negotiating an abatement programme which will include control of odour emissions.

INTRODUCTION

Air quality studies in the town of Dryden were first undertaken by the Ontario Ministry of the Environment in 1970. The results of these investigations have appeared in a series of reports (1, 2, 3) dealing with mercury, particulate fallout, and odour levels around a local kraft pulp mill. The Ministry's 1978 programme, described in this report, included vegetation and soil studies, a snow sampling survey and the operation of a small air quality monitoring network.

VEGETATION AND SOIL ASSESSMENT

Sampling conducted in 1976 and 1977 (2, 3) showed that mercury in vegetation declined sharply following conversion of the mill's chlor-alkali plant to a non-mercury process. To further document the situation, sampling of vegetation and soil was repeated in 1978.

In August, triplicate samples of trembling aspen (*Populus tremuloides*) or Manitoba maple (*Acer negundo*) foliage were collected at 17 sites in Dryden (Figure 1) plus two controls distant from the mill. Surface soil, to a depth of 5 cm (centimetres) was also obtained at the same locations. Sampling and sample processing procedures are described in the 1977 report (3). Analysis for mercury in vegetation and soil was carried out at the Ministry's Thunder Bay laboratory.

There was no evidence of air pollution injury to vegetation except for a small area near site 4, close to the mill. Manitoba maple at this location displayed moderate to severe symptoms of foliar injury very similar to those attributed to emissions from a kraft pulp mill in Fort Frances. An infestation of forest tent caterpillar earlier in the growing season had also caused

light to moderate injury to trembling aspen and trace injury to Manitoba maple foliage at site 4 and most other sampling locations.

Mercury concentrations in vegetation in 1978 (Table 1, Figure 2) were very similar to those reported for 1977. The persistence of slightly elevated mercury indicated that the chlor-alkali plant or pulp mill was a possible weak source of residual airborne mercury. Concentrations at two sites, both on company property, marginally exceeded the Ministry guideline of 100 ng/g (nanograms of mercury per gram of dried vegetation). Mercury levels in soil (Figure 3) were also similar in 1977 and 1978, and two on-property values were found to be over the contaminant guideline (300 ng/g).

Small quantities of *Sphagnum* moss were set out on July 10 at 22 sites around the mill (Figure 4) to test for the presence of airborne pollutants. Details of the technique are outlined in the 1976 report (2). The moss was collected on October 2, after an 84-day exposure period, and analysed for calcium, chloride, mercury and sodium at the Ministry's Thunder Bay and Toronto laboratories. The analytical data are summarized in Table 2, where comparable values for 1976 are also included.

Except at two sites adjacent to the chemical plant, mercury levels in moss were near background concentrations throughout the study area. Sodium was elevated at some locations, but the mill could not be implicated as the source of all the high concentrations. Calcium and chloride levels, on the other hand, clearly showed distribution patterns (Figures 5 and 6) which indicated the mill to be an emission source of these two contaminants. Calcium, chloride and sodium levels were much higher in moss exposed in 1978, when the mill was operating, than in the summer of 1976, when the mill was closed.

SNOW SAMPLING

Snow sampling surveys are useful in detecting the identity and extent of particulate fallout near some industries. Past snow studies at Dryden have shown that calcium, mercury, sodium and sulphate levels have been well above normal background concentrations.

In February, 1978, core samples of the total snow profile were obtained from 20 sites around the mill, plus controls. Sample processing and analytical procedures, carried out at the Ministry's Thunder Bay laboratory, were the same as those used before (2).

Chemical analysis results, in Table 3, showed that calcium levels, while substantially reduced from 1977, still exceeded the guideline in a small area near the mill (Figures 7a and 7b). Mercury levels were similar for the two years, and well below the contaminant guideline. Figures 8a and 8b illustrate the very sharp drop in local mercury deposition from 1975 to 1978. Sodium (Figures 9a and 9b) and sulphate both showed very substantial reductions from 1977 to 1978, following the installation of new dust collection equipment to reduce emissions from the mill's recovery furnace.

Snow meltwater pH varied from 10.8 near the mill to about 4.6 at the control sites. Except for trace amounts of black particulate matter at sites closest to the mill, no visible contaminants were found in samples collected in the 1978 survey.

AIR QUALITY MONITORING

DUSTFALL

Dustfall, which constitutes particulate matter that settles out of the atmosphere by gravity, has been monitored in Dryden since 1973. The method of measurement is described in the 1977

report (3). All total dustfall determinations, and analyses of soluble calcium, chloride, sodium, and sulphate in dustfall were performed at the Ministry's Thunder Bay laboratory.

Table 4 presents the dustfall data for 1978 at the seven sites shown in Figure 10. Except at station 61026, most monthly dustfall complied with the Ontario air quality objective. Dust from nearby unpaved laneways was suspected as the cause of elevated readings at station 61026 (56 King Street). The isolated high reading in September at station 61022 (Earl and Albert) was attributed to dust from construction activity at an adjacent arena. Annual averages were acceptable at three locations, and slightly above the objective at the other four sites. The distribution of the dustfall averages for 1978 in the town area (Figure 11) indicates that the mill was not a significant source of particulate fallout. Vehicular traffic and commercial activity probably accounted for much of the dustfall recorded in the town centre, south of Highway #17. Levels of soluble calcium, chloride, sodium and sulphate in dustfall were consistently very low (usually <0.5 grams per square metre) and well within normal background values at all locations. Trace amounts of black particulate matter were occasionally observed in dustfall jars at the four monitoring points south of Highway 17.

A comparison between average dustfall in 1976, 1977 and 1978 (Table 5) shows that particulate fallout decreased by about 44 percent over a 2-year period.

SULPHATION RATES

Monthly sulphation measurements provide a semi-quantitative estimate of average levels of sulphur-containing gases in the atmosphere. The method, based on the reaction of sulphur compounds with lead dioxide to form lead sulphate, produces a reading when any reactive sulphur compound is present in sufficient concentration.

As well as being non-specific in pollutant identification, the method is further limited by the influence of variations in temperature, wind and humidity. Despite these disadvantages, sulphation monitoring indicates whether airborne sulphur levels are significant and assists in determining long-term trends.

Sulphation rates in Dryden for 1978 (Table 6) were similar to those for 1977. The gradient of decreasing average rates with increasing distance from the mill (Figure 12) indicates that the mill is a source of airborne sulphur. Limited Ministry experience in attempting to establish a relationship between sulphation rates and average concentrations of total reduced sulphur suggests that sulphation rates exceeding 0.20 mg SO_3/100 cm^2/day represent unacceptably high odour levels. Many of the 1978 values in Dryden were well above this guideline.

TOTAL REDUCED SULPHUR

Total reduced sulphur (TRS) comprises a group of sulphur-containing gases which are commonly associated with emissions from kraft pulp mills. If present in the air at very low concentrations, they may create very offensive odours. Higher concentrations may darken lead-based paint, cause vegetation injury, or result in temporary health effects such as respiratory irritation or nausea.

Since early 1977, the Ministry has monitored TRS in Dryden at 56 King Street, about 600 metres east of the mill. The instrument used throughout this period was a Philips model 9700 coulometric titration analyser, which gives readings in the presence of hydrogen sulphide, methyl and ethyl mercaptan, and dimethyl sulphide, all of which are common components of TRS. In 1978, the monitor yielded 77 percent valid data. Virtually no monitoring was possible during November or December because of instrument malfunction.

TRS concentrations recorded in 1978 are summarized in Table 7 and in Figure 13. For 10 months of the year, there were 400 readings (5.9 percent of the total) above the Ontario guideline of 27 ppb (parts per billion). In 11 months the year before, there were 272 excursions above the guideline. The maximum 1-hour average in 1978 was 479 ppb, nearly 18 times the maximum acceptable level. Some unusually high concentrations occurred in August, September and October. An analysis of TRS levels and wind direction for the period April to August (Table 8) showed that all the significant odour concentrations were recorded with westerly and southwesterly winds from the mill.

TRS levels above 50 ppb may give rise to odour complaints, and concentrations above 100 ppb are sometimes associated with signs of temporary discomfort in susceptible individuals. Symptoms may include breathing difficulties, eye irritation, nausea and sleep loss. Such effects are, however, temporary and disappear when TRS concentrations decrease because of reduced emissions or a change in wind direction. There is no evidence of chronic health problems caused by community exposure to TRS compounds in areas near kraft pulp mills. The Ministry is currently negotiating an abatement programme with mill management to significantly reduce TRS emissions and thereby resolve the remaining significant air quality problem in Dryden.

ACKNOWLEDGEMENT

The Ministry wishes to thank staff of the Dingwall Medical Group, Dryden, for assistance in operating the TRS monitor.

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1. Griffin, H. D. 1976. Air quality, Dryden. Annual Report, 1975. Ontario Ministry of the Environment.

2. Ontario Ministry of the Environment. 1977. Air quality, Dryden. Annual Report, 1976.

3. Ontario Ministry of the Environment, 1978. Air quality, Dryden. Annual Report, 1977.

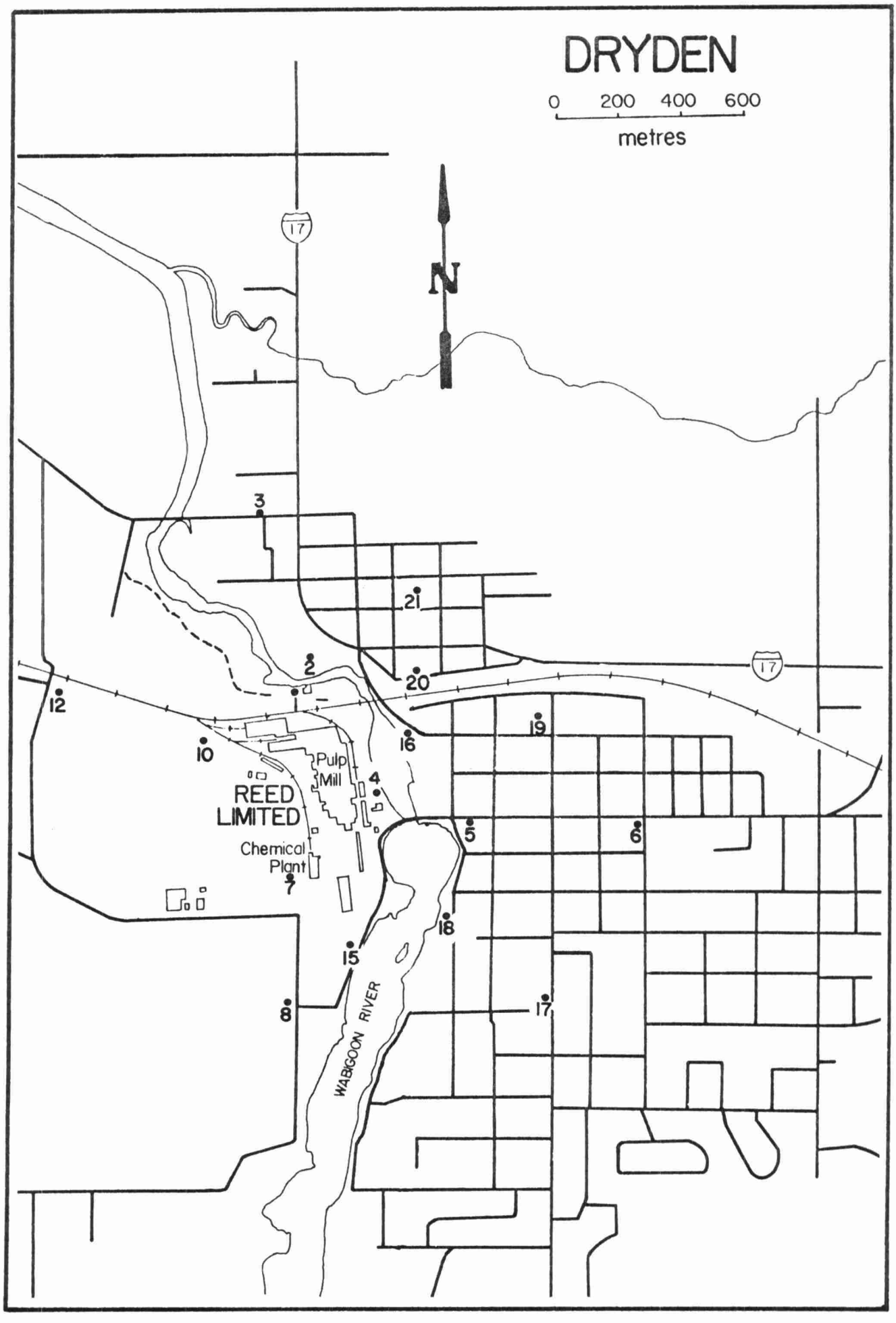

Figure 1. Vegetation and soil sampling sites, 1978.

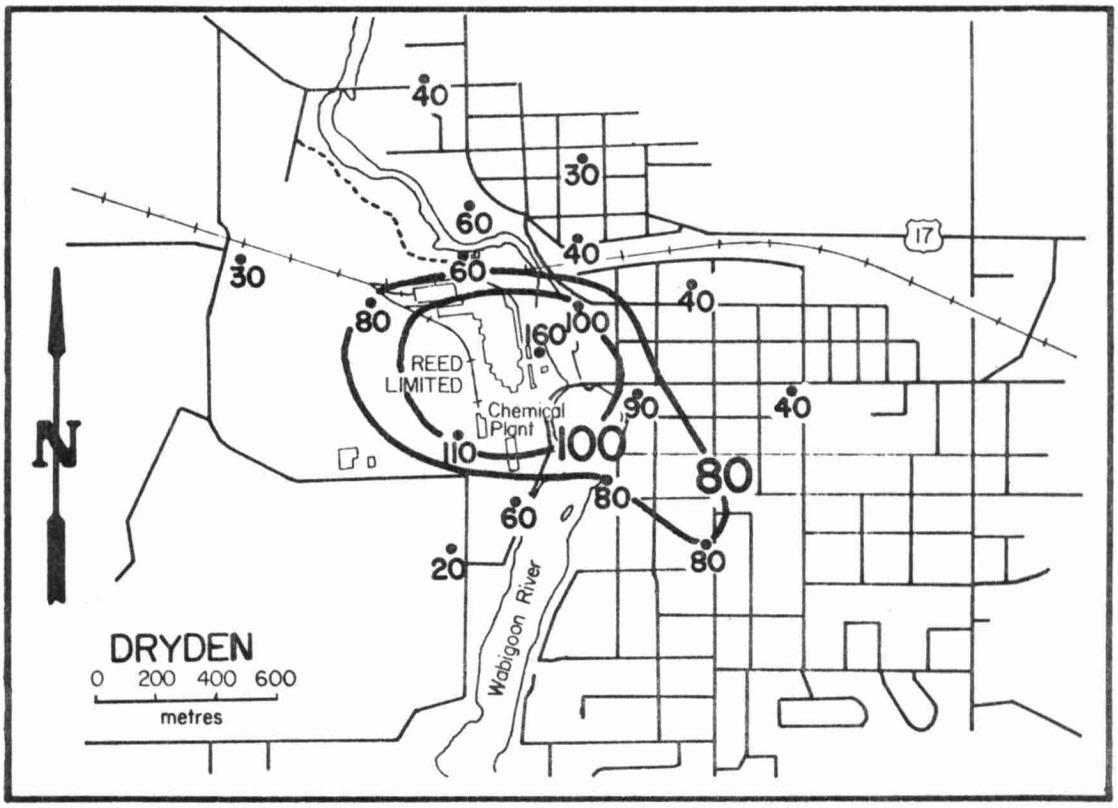

Figure 2. Average mercury concentrations (ng/g, dry weight) in vegetation, August, 1978.

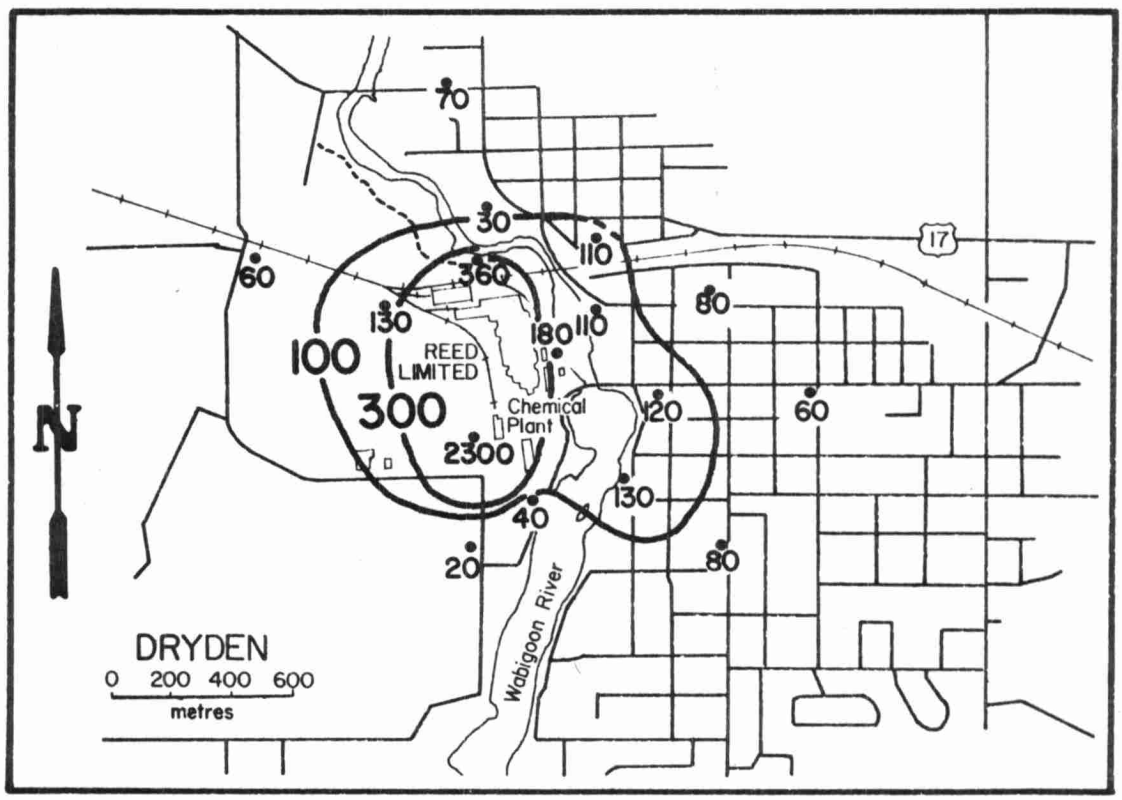

Figure 3. Average mercury concentrations (ng/g, dry weight) in surface soil (0-5 cm), August, 1978.

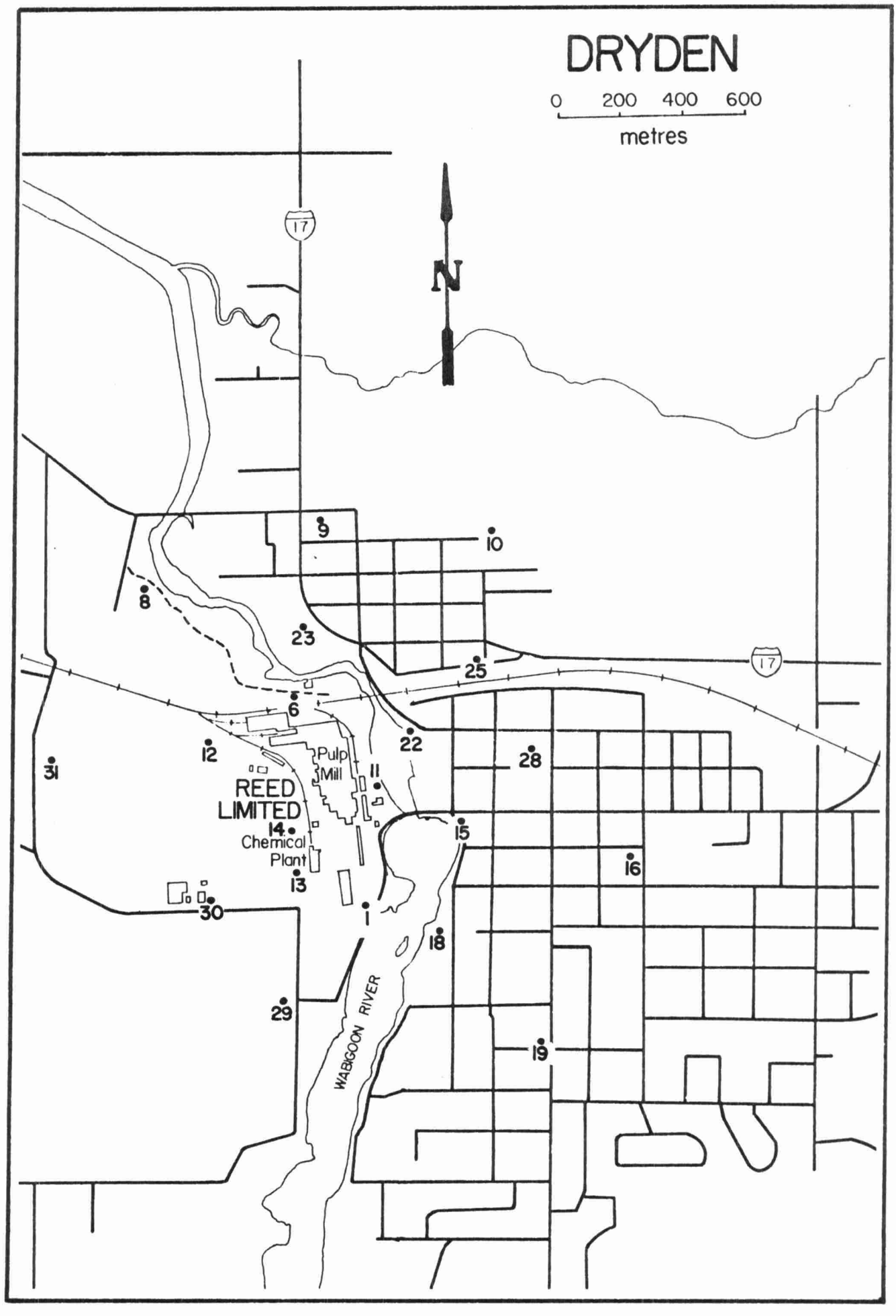

Figure 4. Moss bag exposure sites, 1978.

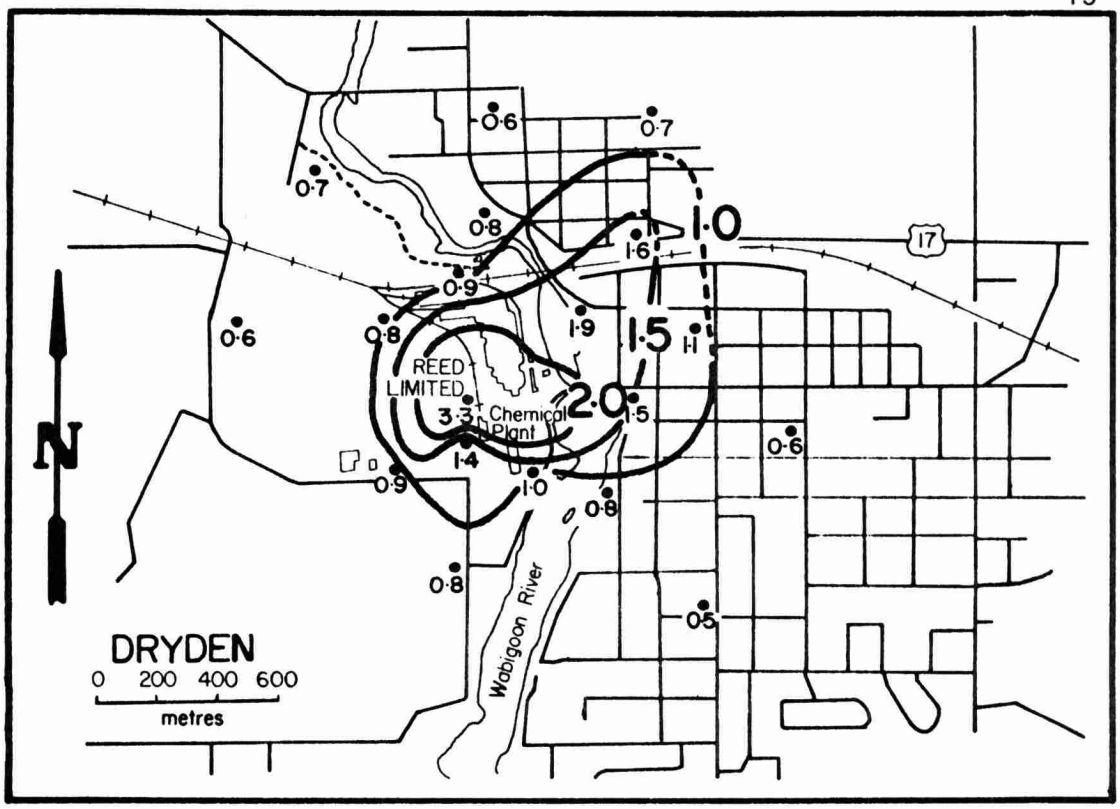

Figure 5. Calcium levels (percent, dry weight) in moss exposed July 10 to October 2, 1978.

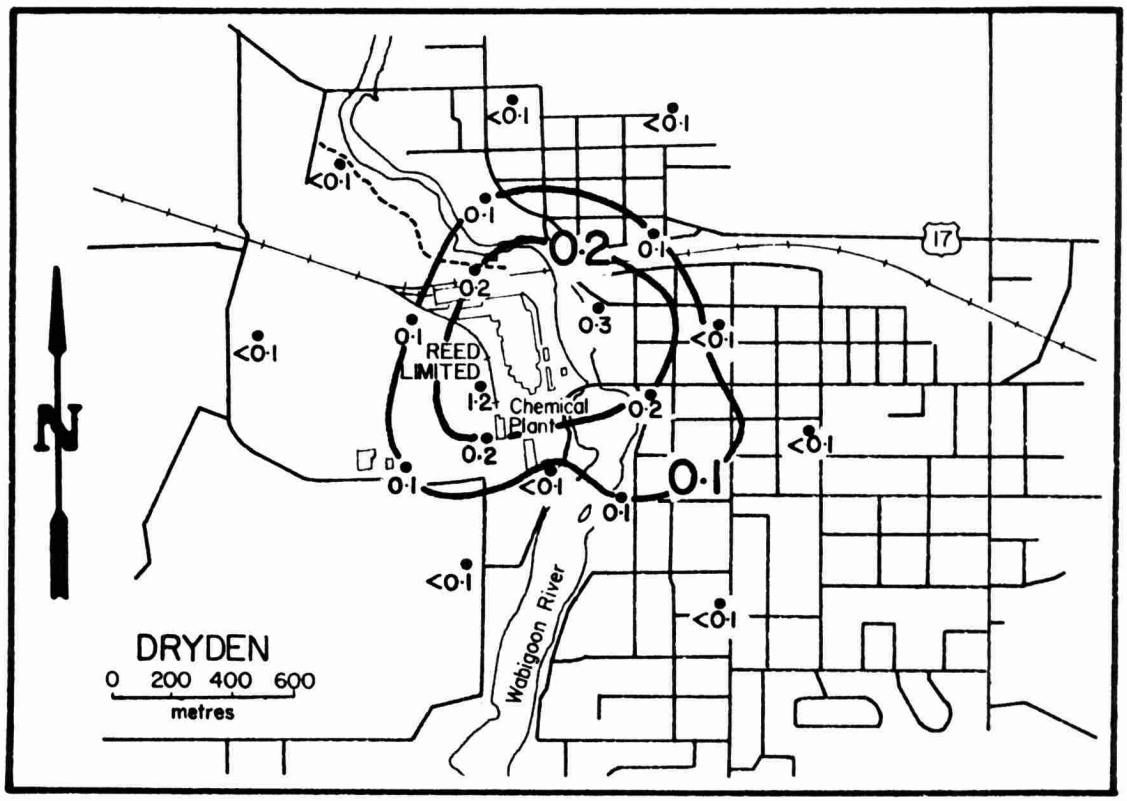

Figure 6. Chloride levels (percent, dry weight) in moss exposed July 10 to October 2, 1978.

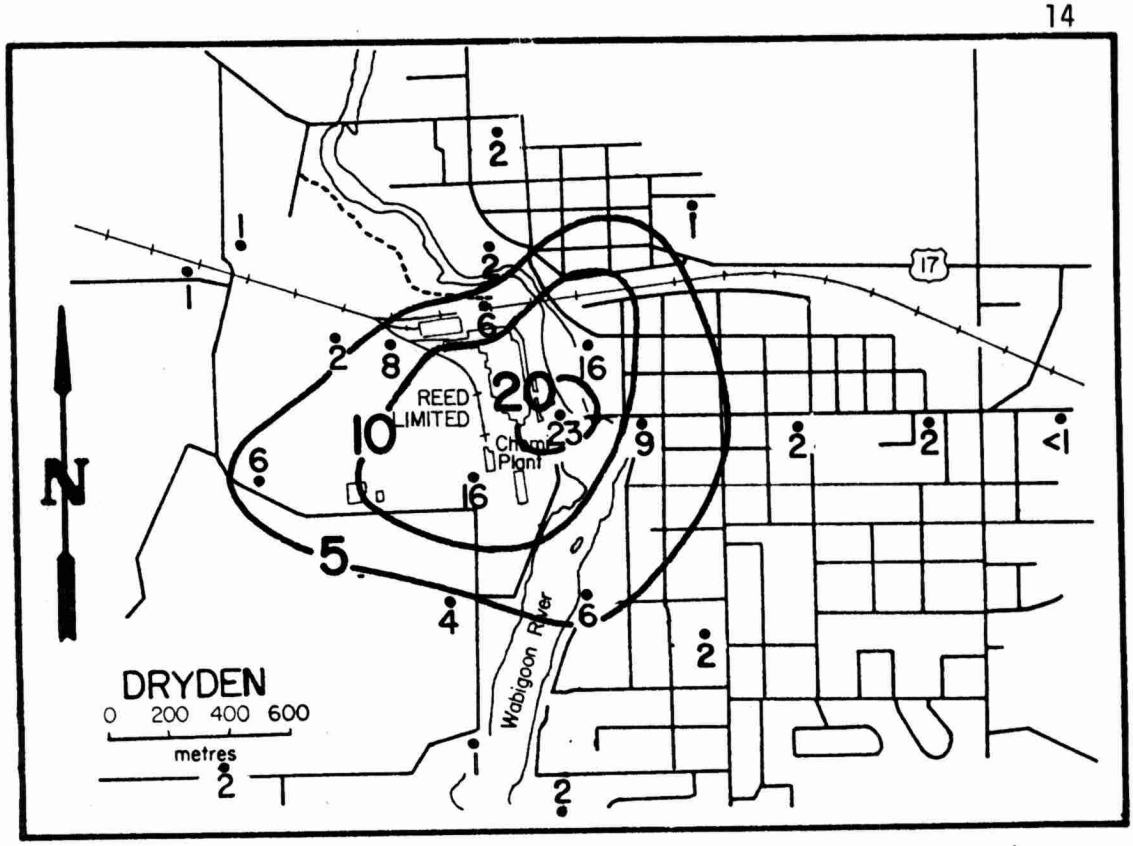

Figure 7a . Average concentrations of calcium (mg/l) in snow, March, 1977.

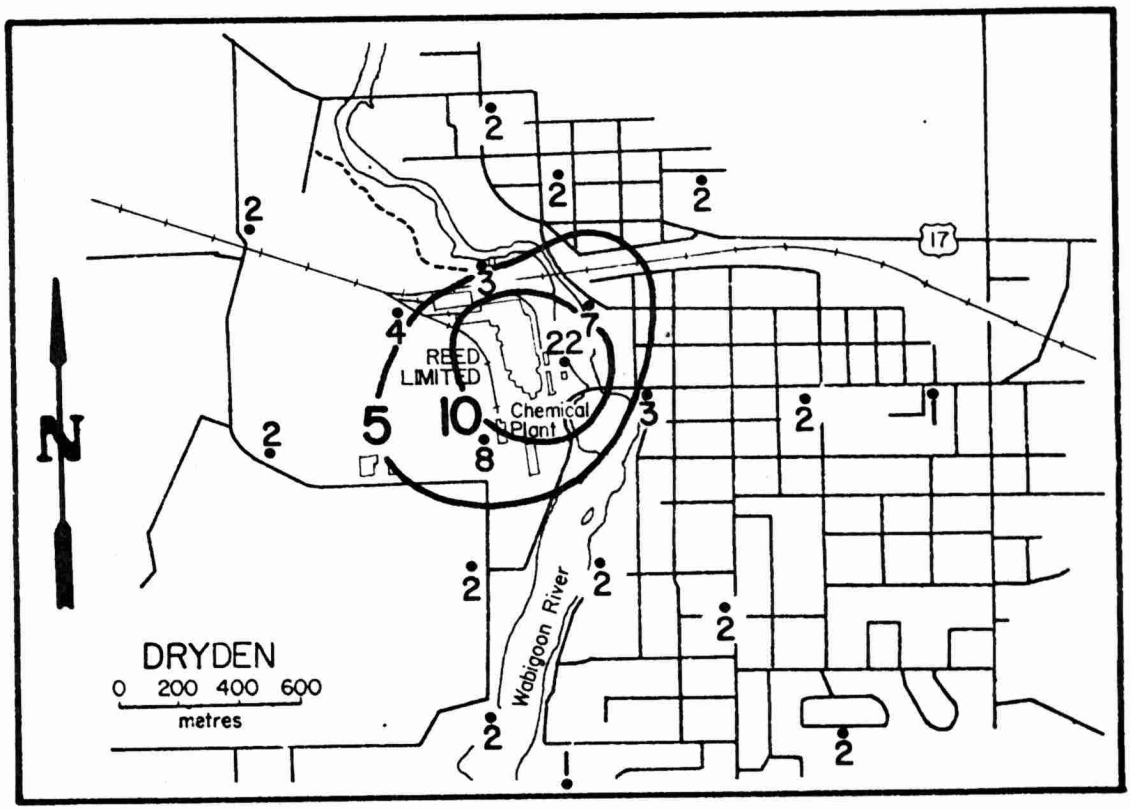

Figure 7b. Average concentrations of calcium (mg/l) in snow, February, 1978.

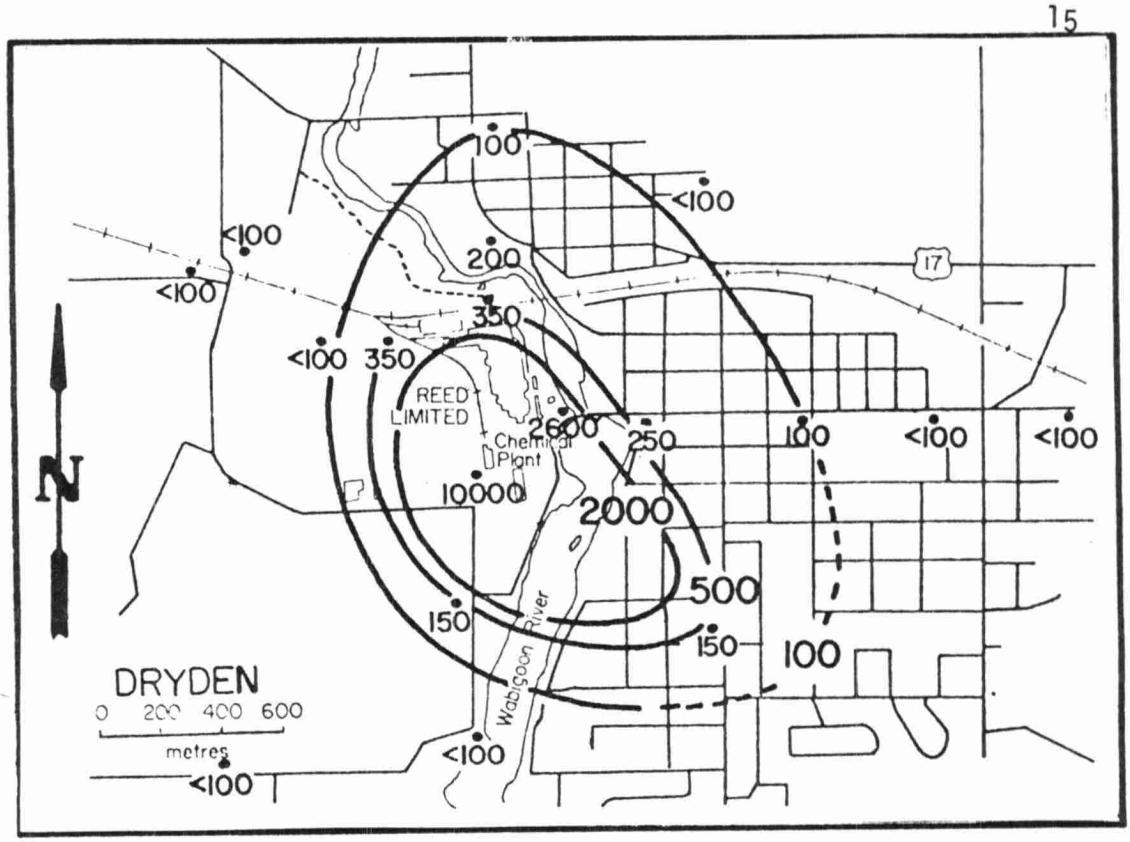

Figure 8a. Average concentrations of mercury (ng/l) in snow, January and March, 1975.

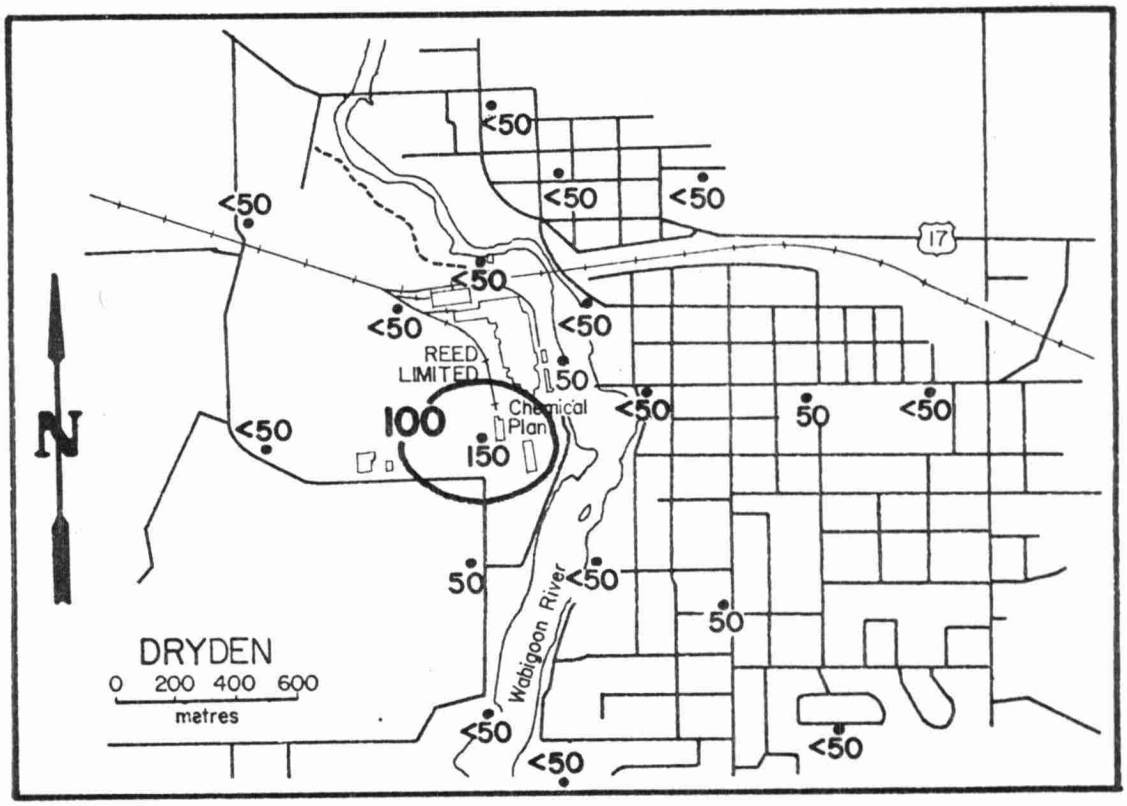

Figure 8b. Average concentrations of mercury (ng/l) in snow, February, 1978.

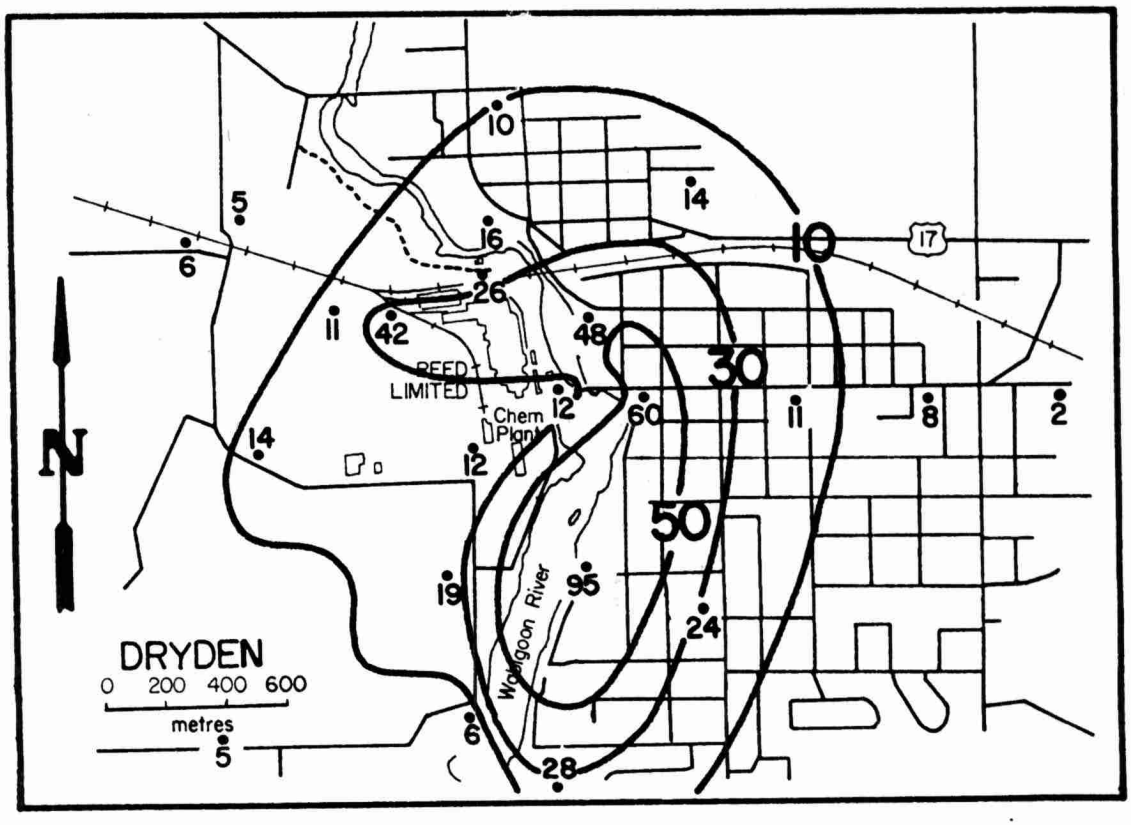

Figure 9a. Average concentrations of sodium (mg/l) in snow, March, 1977.

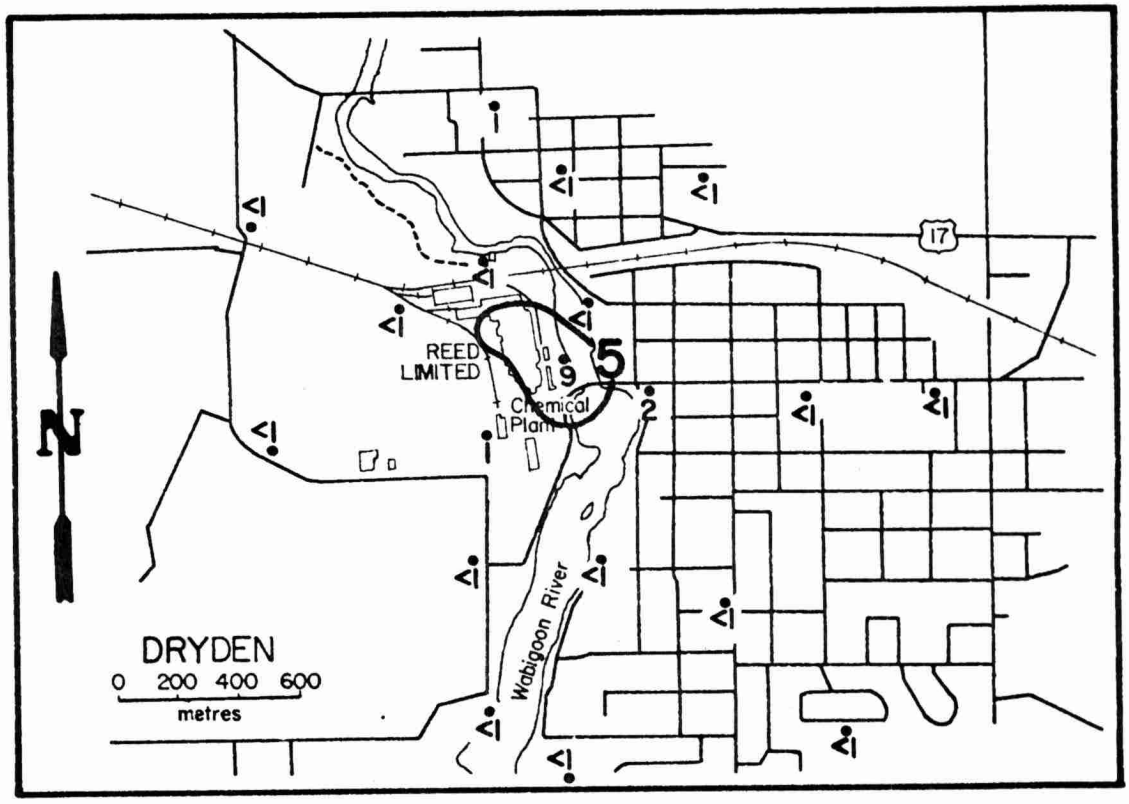

Figure 9b. Average concentrations of sodium (mg/l) in snow, February, 1978.

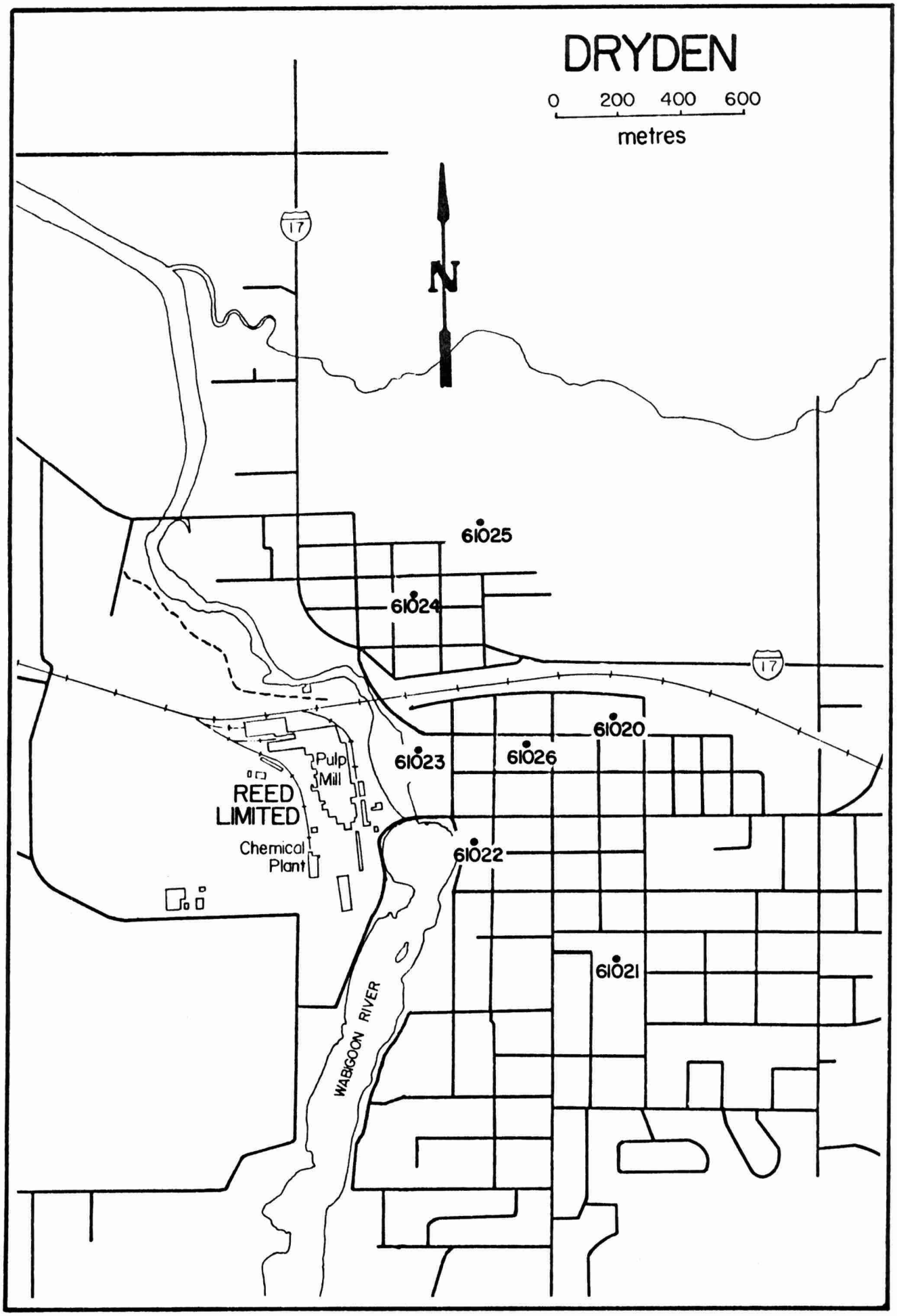

Figure 10. Air quality monitoring sites, 1978.

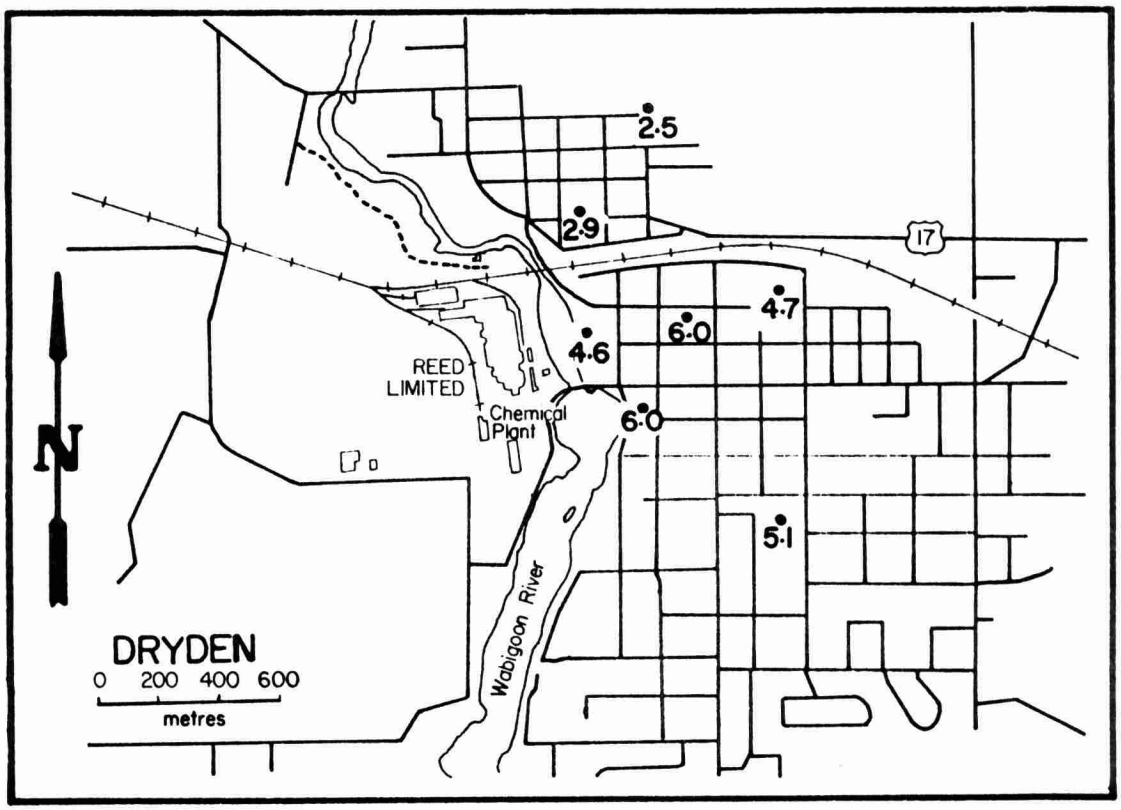

Figure 11. Average dustfall (g/m^2/ 30 days) , 1978.

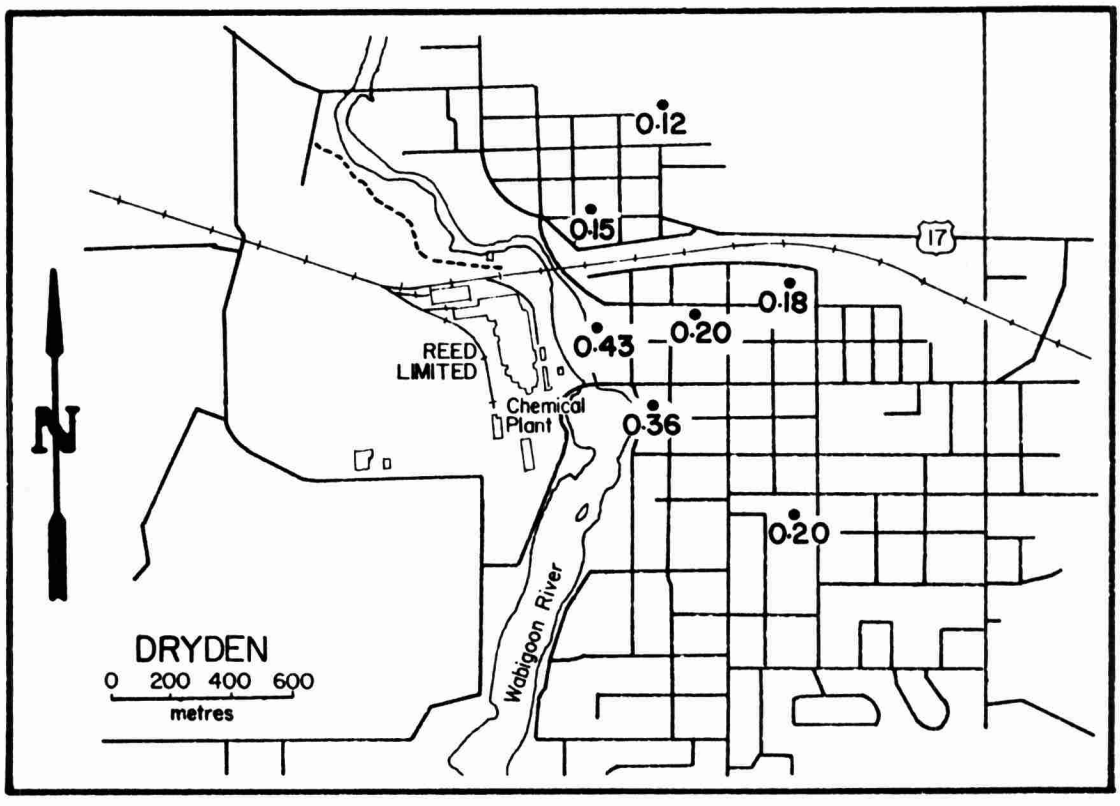

Figure 12. Average sulphation rate (mg SO_3/100 cm^2/day), 1978.

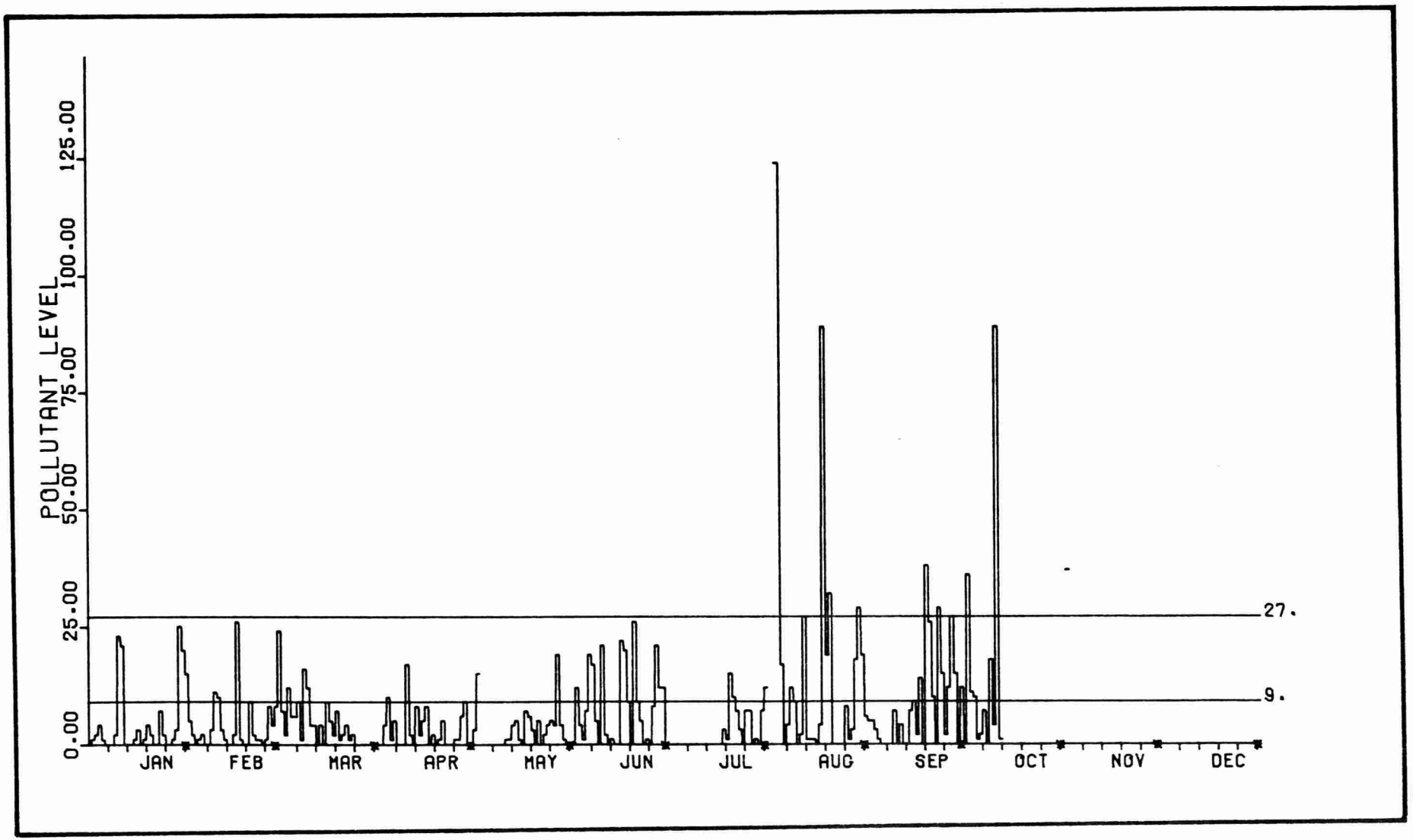

Figure 13. Daily mean TRS concentrations (parts per billion), station 61026, Dryden, 1978.

TABLE 1. Average mercury concentrations (μg/g, dry weight) in triplicate samples of vegetation[a] and surface soil in Dryden, 1975 to 1978.

Site	Vegetation				Soil (0-5 cm)			
	1975	1976	1977	1978	1975	1976	1977	1978
1	1840	100	80	60	140	50	340	360
2	1400	110	80	60	40	70	50	30
3	510	180	90	40	30	30	40	70
4				160	250	390	470	180
5			80	90	110	130	90	120
6			50	50	140	50	50	60
7	460	650	210	110	1200	1900	1300	2300
8	50	50	40	20	50	30	30	20
9	60	60	50		50	40	40	
10	510	160	60	80	200	340	270	130
11	380	90	60		180	300	120	
12	140	30	40	30	70	100	110	60
15		120	60	60		370	50	40
Controls	20	30	20	20	50	20	40	40

[a]Manitoba maple or trembling aspen.

TABLE 2. Comparison between concentrations, dry weight basis, of calcium, chloride, mercury and sodium in moss exposed in 1976 and 1978[a].

Site	Calcium (%)		Chloride (%)		Mercury (ng/g)		Sodium (µg/g)	
	1976	1978	1976	1978	1976	1978	1976	1978
1	0.08	1.00	0.04	0.05	70	130	120	530
6	0.15	0.88	0.04	0.16	30	140	180	610
8	0.09	0.68	0.02	0.06	100	100	50	130
9	0.10	0.62	-	0.05	80	100	110	490
10	0.09	0.66	0.02	0.03	10	110	110	440
11	0.14	-	0.02	-	80	-	135	-
12	0.31	0.79	0.02	0.10	820	120	205	890
13	0.08	1.40	0.08	0.17	120	240	110	910
14	0.16	3.30	0.02	1.25	1500	940	260	3100
15	0.25	1.50	0.02	0.25	150	110	280	1600
16	0.01	0.60	0.04	0.05	60	100	180	380
18	<0.01	0.78	0.02	0.10	<10	110	215	560
19	0.01	0.49	0.02	0.02	<10	110	190	1600
22	0.14	1.90	0.02	0.28	40	140	305	1300
23	0.09	0.82	0.03	0.10	50	120	75	930
25	0.03	1.60	0.02	0.14	<10	150	125	810
28		1.10		0.08		130		580
29		0.76		0.03		90		290
30		0.93		0.12		140		1600
31		0.60		0.03		100		420
Controls	0.12	0.15	0.02	<0.02	<10	140	155	130

[a]1976 values are averages of two exposure periods (July 13-August 17, August 17-September 13).
1978 values are for one exposure period (July 10-October 2).

TABLE 3. Average levels of calcium, mercury, sodium, sulphate and pH in meltwater from snow samples collected in Dryden in March, 1977 and February, 1978.

Distance (metres) and direction from source[a]	Calcium (mg/l)		Mercury (ng/l)		Sodium (mg/l)		Sulphate (mg/l)		pH	
	77	78	77	78	77	78	77	78	77	78
350 N	6	3	<50	<50	26	<1	67	3	8.4	6.0
635 NNE	-	2	-	<50	-	<1	-	1	-	8.6
865 N	2	2	<50	<50	10	1	19	1	6.2	7.8
1455 N	1	2	<50	<50	4	1	7	<1	5.4	7.2
320 NE	16	7	70	<50	48	1	86	2	8.8	9.4
930 NE	1	2	<50	<50	14	<1	34	1	5.8	7.7
190 E	23	22	<50	50	12	9	20	4	9.4	10.8
415 E	9	3	<50	<50	60	2	122	2	8.4	9.4
945 E	2	2	<50	50	11	<1	26	1	5.2	9.0
1325 E	2	1	<50	<50	8	<1	18	1	5.2	8.4
655 SSE	6	2	<50	<50	95	<1	205	2	7.3	7.8
990 SE	2	2	<50	50	24	<1	57	2	6.1	8.3
1600 SSE	-	2	-	<50	-	<1	-	2	-	8.2
255 SSW	16	8	460	150	12	<1	25	2	9.5	9.4
690 SSW	4	2	<50	50	19	<1	52	1	6.2	8.8
1090 S	1	2	<50	<50	6	<1	18	1	4.9	8.5
1410 S	2	1	<50	<50	28	<1	75	1	6.6	7.4
870 WSW	6	2	<50	<1	14	<1	26	2	8.1	8.9
300 W	8	4	70	<1	42	<1	82	1	9.0	6.2
1000 NW	1	2	<50	<50	5	<1	11	<1	5.2	7.6
Controls	<1	<1	<50	<50	<1	<1	1	<1	4.0	4.6
Guideline	5		500		10		10			

[a]Source arbitrarily designated as recovery furnace stack, Reed Limited kraft pulp mill.

TABLE 4. Total dustfall (g/m^2/30 days), Dryden, 1978.

Station	Location	Distance (metres) and direction from source[a]	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
61020	Kirkpatrick/Queen	895 ENE	0.4	1.5	3.2	5.1	8.6[b]	8.1	8.2	4.7	6.1	4.4	4.2	1.7	4.7
61021	Casimir/St. Charles	1010 ESE	1.5	-	6.1	7.8	6.4	2.7	3.9	3.9	5.4	8.0	-	-	5.1
61022	Earl/Albert	430 ESE	0.6	1.5	6.3	7.8	4.3	4.7	4.7	-	28.4	4.0	2.1	1.8	6.0
61023	King/Wabigoon River	305 NE	0.7	1.7	3.7	6.4	6.2	6.3	-	8.6	8.5	2.9	3.9	2.2	4.6
61024	Mary/Florence	735 NNE	0.3	1.6	2.7	-	4.5	4.4	4.1	3.9	3.5	2.2	2.6	1.6	2.9
61025	Park/Second	960 NNE	-	1.1	1.0	4.0	2.5	5.3	2.4	1.5	2.4	1.3	4.6	0.9	2.5
61026	56 King Street	625 ENE	1.6	1.3	4.1	7.6	5.8	7.5	8.2	9.4	13.0	8.0	4.1	1.5	6.0

[a]Source arbitrarily designated as recovery furnace stack, Reed Limited kraft mill.

[b]Values exceeding maximum acceptable levels of 7.0 (monthly) or 4.6 (annual average) are underlined.

TABLE 5. Comparison between average annual dustfall (g/m^2/30 days) at Dryden in 1976, 1977 and 1978.

Year	Station						All stations
	61020	61021	61022	61023	61024	61025	
1976	8.0	6.3	9.8	11.5	5.9	4.5	7.7
1977	5.8	7.7	7.4	8.5	6.0	3.2	6.4
1978	4.7	5.1	6.0	4.6	2.9	2.5	4.3

TABLE 6. Sulphation rates (mg $SO_3/cm^2/day$), Dryden, 1978.

Station	Location	Distance (metres) and direction from source[a]	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
61020	Kirkpatrick/Queen	895 ENE	.20	.10	.17	.04	.06	.34	.08	.40	.14	.25	-	.11	.18
61021	Casimir/St. Charles	1010 ESE	.23	.28	.26	.22	.05	.22	.16	.32	.16	.18	.19	.09	.20
61022	Earl/Albert	430 ESE	.26	.49	.23	.23	.12	.34	.33	.69	.48	.47	.45	.20	.36
61023	King/Wabigoon River	305 NE	.39	.21	.49	.12	.23	.89	.26	.79	.52	-	.45	.41	.43
61024	Mary/Florence	735 NNE	.15	.07	.10	.04	.03	.37	.17	.27	.22	-	.19	.09	.15
61025	Park/Second	960 NNE	.17	.04	.08	.02	.02	.29	.21	.22	-	-	.13	.07	.12
61026	56 King Street	625 ENE	.20	.14	.19	.09	.08	.43	.11	.40	.22	-	.22	.19	.20

[a]Source arbitrarily designated as recovery furnace stack, Reed Limited kraft mill.

TABLE 7. Distribution of total reduced sulphur readings (ppb, hourly averages) in 1978 at station 61026, Dryden.

Month	Days of data	Number of readings for concentrations of: 0-10	11-27	28-50	51-100	101-300	300-500	Maximum value: Hourly	Daily
Jan	31	660	37	27	9	3	0	135	25
Feb	28	609	41	9	6	1	0	140	26
Mar	31	635	69	21	9	1	0	102	24
Apr	30	660	38	8	7	1	0	103	17
May	30	657	35	17	9	0	0	77	19
Jun	30	580	74	30	23	6	0	140	26
Jul	31	693	30	12	8	0	0	91	15
Aug	28	549	54	30	17	40	0	269	124
Sep	30	587	61	26	29	6	0	233	38
Oct	12	241	34	5	8	12	2	352	89
Nov	1	18	0	1	4	7	6	479	37
Dec				no data					
YEAR	282	5889	474	186	129	77	8	479	124

TABLE 8. Directional distribution of hourly readings of total reduced sulphur (TRS) in 1978 at station 61026, Dryden.

Wind direction[a]	Number of hours of wind, by direction[b]	Average TRS concentration (ppb)
N	132	0.7
NNE	170	0.8
NE	132	0.4
ENE	120	0.2
E	95	0.1
ESE	80	0.1
SE	108	0.4
SSE	177	0.4
S	298	1.6
SSW	213	12.4
SW	172	24.8
WSW	120	40.0
W	191	10.5
WNW	126	3.4
NW	93	0.7
NNW	107	1.3
Calm	63	5.8

[a]Measured 10 m above ground at Dryden airport.
[b]April to August, 1978.